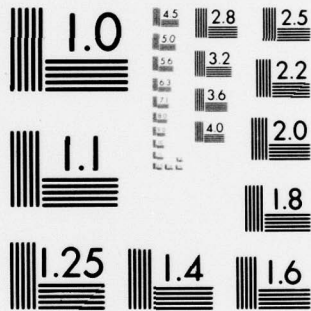MICROCOPY RESOLUTION TEST CHART
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NEW CONDUCTIVE POLYMERIC MATERIALS: COFACIAL ASSEMBLY OF MIXED VALENT METALLOMACROCYCLES.

by

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Bhagyashree R. Kundalkar

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper reports on an approach to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a cofacial orientation. Iodine doping of the face-to-face linked oligomers $[M(Pc)O]_n$ (M=Si, Ge, Sn; Pc = phthalocyaninato) produces electrically conductive polymers $\{[(M(Pc)O]I_x\}_n$ with a wide range of x stoichiometries. Resonance Raman spectroscopy

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indicates that the iodine has oxidized the polymer chain. Polymer structure has been studied by X-ray powder diffraction, and it is possible to estimate interplanar spacings. Halogen doping of the $[M(Pc)O]_n$ materials is accompanied by electrical conductivity increases as large $10^7(ohm\ cm)^{-1}$; the general trend is $\sigma_{Si} \gtrsim \sigma_{Ge} > \sigma_{Sn}$. Variable temperature conductivity and magnetic susceptibility data are reported.

SIGMA

10 To the 7th power (ohm cm)

NEW CONDUCTIVE POLYMERIC MATERIALS:
COFACIAL ASSEMBLY OF MIXED
VALENT METALLOMACROCYCLES.

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Abstract

This paper reports on an approach to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a cofacial orientation. Iodine doping of the face-to-face linked oligomers $[M(Pc)O]_n$ (M=Si, Ge, Sn; Pc = phthalocyaninato) produces electrically conductive polymers $\{[M(Pc)O]I_x\}_n$ with a wide range of x stoichiometries. Resonance Raman spectroscopy indicates that the iodine has oxidized the polymer chain. Polymer structure has been studied by X-ray powder diffraction, and it is possible to estimate interplanar spacings. Halogen doping of the $[M(Pc)O]_n$ materials is accompanied by electrical conductivity increases as large 10^7 (ohm cm)$^{-1}$; the general

trend is $\sigma_{Si} \gtrsim \sigma_{Ge} > \sigma_{Sn}$. Variable temperature conductivity and magnetic susceptibility data are reported.

Substantial progress has been achieved over the past several years in understanding how organic and metal-organic molecular solids can be imbued with metal-like charge transport properties.[2] Two features now appear to be requisite for facile charge conduction. First, the molecules must be arrayed in close spacial proximity and in crystallographically similar environments (e.g. molecular stacks). Second, these molecules must exist in formal fractional oxidation states ("mixed valence", "incomplete charge transfer", "partial oxidation"). Our understanding of the importance and workings of these factors is presently at a very qualitative level. Even worse, our ability to test these ideas or to rationally manipulate the various parameters via chemical synthesis is at an extremely primitive stage of development. For example, those molecular and intermolecular forces which govern whether stacks[3] form, whether stacks are segregated ("homosoric" [3e]) or integrated ("heterosoric" [3e]), whether stacks consist of D_{nh} or canted arrays, and how stacks are oriented with respect to electron donors and acceptors[3], are not well-understood and almost impossible to control. In this paper we report on a new, successful approach to the control of molecular stacking and lattice architecture in low-dimensional mixed valence materials. This approach involves the assembly and partial oxidation of well-characterized and chemically flexible subunits. As such, it capitalizes on a great deal of accumulated knowledge, and offers the

possibility of constructing a large variety of conductive polymers with well-defined and readily manipulatable primary and secondary structures . This approach also offers the possibility of modifying various aspects of the lattice dynamics which are involved in Peierls transitions[2] and other electron-phonon coupling phenomena.[2,4]

Work in our laboratory[5,6] and elsewhere[7] has previously shown that one viable route to conductive molecular solids is the halogen oxidation of planar, conjugated metallomacrocycles. Although this approach is greatly weakened by inability to enforce molecular stacking, in cases where stacks do form, it is known that the metal-ligand units can frequently be brought into fractional oxidation states. Moreover, the form of the halogen acceptor (A) present (A^-, A_3^-, A_5^-, A_2) can be readily deduced using resonance Raman and Mössbauer spectroscopy.[8] This allows rapid and accurate assessment of the degree of incomplete charge transfer. We now apply this successful oxidative methodology to systems in which the metallomacrocyclic units are joined by strong covalent linkages with bond energies on the order of 80-100 kcal (ca. 3.5-4.5 eV)/mole. Thus, the degree of stacking control is necessarily far greater than in simple stacked systems where weaker covalent bonding is evidenced by bandwidths on the order of only ca. 10 kcal (0.5 eV)/mole[2]. Although we illustrate here with one particular class of metallomacrocycle subunit (the technologically important[9] phthalo-

cyanine, Pc) and one type of linking atom (oxygen), the generalizability of this approach should be evident.

Experimental

The compounds $Si(Pc)Cl_2$, $Ge(Pc)Cl_2$, and $Sn(Pc)Cl_2$ were synthesized by the literature procedure[10] or by a new "one-pot" method.[11] The dichlorides were next hydrolyzed in pyridine/NaOH[12] to yield the corresponding dihydroxides, $Si(Pc)(OH)_2$, $Ge(Pc)(OH)_2$, and $Sn(Pc)(OH)_2$. Condensation[10,13] of the monomers was then carried out by dehydration at 300-400° $C/10^{-3}$ torr to produce the polymers $[Si(Pc)O]_n$, $[Ge(Pc)O]_n$, and $[Sn(Pc)O]_n$ in high yield and purity. The polymer $[Si(Pc)O(\underline{p}\text{-}C_6H_4O)]_n$ was prepared from $Si(Pc)Cl_2$ and hydroquinone by the literature procedure.[13b] Halogen doping was achieved by reacting the powdered polymers with solutions of the appropriate halogens or with halogen vapor. Stoichiometry was determined by elemental anaysis.

Charge transport measurements were performed on compressed, polycrystalline pellets using standard four-probe ac or dc van der Pauw methods.[14] X-ray powder diffraction studies were carried out with a Picker 6147 diffractometer using filtered $CrK\alpha$ radiation. Resonance Raman spectra were obtained on spinning samples using $Ar^+(5145 Å)$ excitation. Static magnetic susceptibility studies were performed with a Faraday balance using $HgCo(SCN)_4$ as a calibrant. Appropriate corrections were made for diamagnetism.

Results and Discussion

Dehydration of dihydroxy silicon, germanium, and tin phthalo-
cyanines produces phthalocyaninato polysiloxane, polygermyloxane,
and polystannyloxane materials[10, 13] in which the macrocycles are rigidly
held in a face-to-face configuration. This geometry is illustrated
in Figure 1. In the case of M = silicon, the backbone of the polymer
is the well-known, robust silicone structure.[15] The $[M(Pc)O]_n$ materials are
electrical insulators, however doping with iodine or bromine produces
dramatic increases in the electrical conductivity (Table I). Depending
on the concentrations of reagents employed, the doping can be achieved
over a wide range of stoichiometries, as can be seen in Table I. The
iodinated phthalocyaninato polymers appear to be indefinitely stable to
air and water; the iodine can only be driven off by prolonged heating at
temperatures in excess of 100° C.

The effect of the halogenation on the stack electronic structure has
been investigated by resonance Raman spectroscopy. These studies[5, 8]
reveal the absence of significant quantities of $I_2(\nu = 207 \text{ cm}^{-1})$. Rather,
electron transfer to the halogen has taken place, and the characteristic
scattering pattern of the I_3^- totally symmetric stretching fundamental
(accompanied by the usual overtone progression) is observed at 108 cm^{-1}
(Figure 2). In the case of high iodine concentrations, the 160 cm^{-1}

transition assignable to I_5^- is also detected.[5,8] Thus, the large increase in electrical conductivity can be directly attributed to oxidation of the cofacial macrocyclic array.

It is important before charge transport properties are discussed further, to establish the polymer structure depicted in Figure 1 in greater metrical detail. X-ray powder diffraction patterns of the $[M(Pc)O]_n$ and $\{[M(Pc)O]I_x\}_n$ materials are nearly identical. Furthermore, these patterns can be indexed in the tetragonal crystal system and are very similar to the powder diffraction patterns of $Ni(Pc)I_{1.0}$[6c] and $Ni(dpg)_2I_{1.0}$[5b] (dpg = diphenylglyoximato). These two systems have been studied by single crystal X-ray diffraction techniques and the crystal structures are found to consist of stacks of partially oxidized metallomacrocycle units and chains of polyiodide molecules extending parallel to the $\underline{c}$ direction. The crystal structure of $Ni(Pc)I_{1.0}$ is illustrated in Figure 3. From the single crystal results, the stacking intervals $(\underline{c}/2)$ are found to be 3.244 (3) Å ($Ni(Pc)I_{1.0}$) and 3.271(1) Å. ($Ni(dpg)_2I_{1.0}$). The stacking intervals in the cofacial polymers can be derived from the indexed powder patterns and are found to be 3.33(2) Å (Si-O-Si), 3.51(2) Å (Ge-O-Ge), and 3.95(2) Å (Sn-O-Sn). The reliability of these parameters and support for the $[M(Pc)O]_n / \{[M(Pc)O]I_x\}_n$ structural proposal is supported by several lines of evidence. First, a model for the cofacial metallomacrocycle chain in $[Si(Pc)O]_n$ and

$\{[Si(Pc)O]I_x\}_n$ is derived from the $\{Si(Pc)O\}$ fragment in the molecule $[(CH_3)_3SiO]_2(CH_3)SiO[Si(Pc)O]_3Si(CH_3)[OSi(CH_3)_3]_2$[16]. Here single crystal X-ray diffraction studies reveal linear Pc(Si)-O-(Si)Pc linkages and an interplanar spacing of $3.324(2)\text{Å}$. This result is presented in Figure 4. In regard to the structures of the polygermyloxane and polystannyloxane macromolecules, the powder diffraction-derived interplanar spacings are in favorable agreement with those estimated from ionic radii[17] assuming linear Ge-O-Ge and Sn-O-Sn linkages, i.e. 3.58Å for $[Ge(Pc)O]_n$ and $\{[Ge(Pc)O]I_x\}_n$; 3.90Å for $[Sn(Pc)O]_n$ and $\{[Sn(Pc)O]I_x\}_n$. There is ample precedent for molecules with linear Ge-O-Ge and Sn-O-Sn linkages[18].

As concerns the charge transport data, it can be seen (Table I) that the general trend in conductivity is $\sigma_{Si} \gtrsim \sigma_{Ge} > \sigma_{Sn}$. Since the transport properties of iodine-oxidized metallophthalocyanines are known to be largely ligand-dominated and insensitive to the identity of the metal[6,19], the M dependence of $\{[M(Pc)O]I_x\}_n$ conductivity appears largely to reflect differences in interplanar spacing. Variable temperature studies indicate that the conductivity of the polycrystalline $\{[M(Pc)O]I_x\}_n$ materials is thermally activated (Figure 5) and least-squares fits to equation (1) give the apparent activation parameters compiled in Table I.

$$\sigma = \sigma_0 \, e^{-\Delta/kT} \tag{1}$$

The general trend is $\Delta_{Si} \lesssim \Delta_{Ge} < \Delta_{Sn}$. The doped face-to-face

polymers possess high thermal stability, and samples of the

$\{[Si(Pc)O]I_x\}_n$ materials could be studied to 300° C with only minor

degradation in subsequently measured room temperature conductivity.

To view the magnitude of the $\{[M(Pc)O]I_x\}_n$ conductivities in perspec-

tive, an informative comparison can be made with data for Ni(Pc)I$_{1.0}$

pressed polycrystalline pellets and single crystals. The published

powder parameters for this "molecular metal", σ (300° K) = 0.7

(ohm cm)$^{-1}$, Δ = 0.04 eV,[6b] are comparable to the those of the most

conductive phthalocyaninato polysiloxane and polygermyloxane samples.

As already noted, conductivities of iodinated metallophthalocyanines

are rather insensitive to metal, and the Pc(Ni)-(Ni)Pc distance of

3.244 (3) Å is only slightly greater than the Pc(Si)-O-(Si)Pc distance

of 3.33 (2) Å. Experience indicates that single crystal conductivities

of low-dimensional materials are typically 10^2-10^3 greater along the

molecular stacking axis than as measured for compressed, poly-

crystalline samples, in which conductivity is averaged over all crys-

tallographic directions and is subject to interparticle contact effects.[2,6,20]

Thus, the fact that $\underline{c}$ axis single crystal conductivites of Ni(Pc)I$_{1.0}$

are as high as 600 (ohm cm)$^{-1}$ and obey a $T^{-1.9}$ temperature depen-

dence down to ca. 60° K,[6a] strongly suggests that $\{[Si(Pc)O]I_x\}_n$ and

possibly $\{[Ge(Pc)O]I_x\}_n$ conductivities will be metal-like in the stacking direction.

Further support for a highly delocalized electronic structure in the $\{[M(Pc)O]I_x\}_n$ materials is derived from variable temperature studies of magnetic susceptibility. As is the case for many low-dimensional mixed valence materials,[2, 6b, 21] we find the suscepti-bilities of the $\{[Sn(Pc)O]I_x\}_n$, $\{[Ge(Pc)O]I_x\}_n$, and $\{[Sn(Pc)O]I_x\}_n$ macromolecules to be only modestly paramagnetic at room temp-erature and only weakly dependent on temperature. Representative data are shown in Figure 6. We tentatively attribute increases in susceptibility at low temperature to paramagnetic impurities.

The effect of drastically increasing the interplanar separation has also been investigated. Thus, doping experiments employing the usual iodination procedure were conducted with the silicon phthal-ocyaninato polymer having bridging p-diphenolate linkages as shown below. The interesting result is that only traces of iodine

$$\left[\left(Si\right) - O - (C_6H_4) - O - \right]_n$$
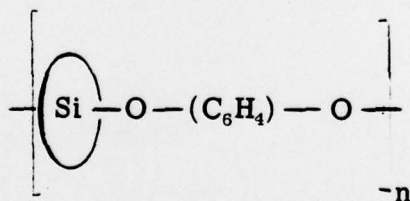
are incorporated, and the resonance Raman spectrum reveals only the presence of I_2. The electrical conductivity remains insulating. Thus, it appears at this stage that the incomplete charge transfer state cannot be attained without a critical proximity and orientation of the arrayed subunits. Further experiments are in progress to better define these requirements, and to relate them to charge transport.

This work represents an initial attempt to learn how to control molecular stacking in low-dimensional mixed valence materials. The approach to this probelm through polymer design offers the possibility of new ways to control and to understand those fundamental factors which govern charge conduction in molecular solids. Furthermore, this strategy offers new ways to tailor materials for optimum performance and processing characteristics.

Acknowledgments

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TABLE I. ELECTRICAL CONDUCTIVITY DATA FOR POLYCRYSTALLINE SAMPLES OF HALOGEN-DOPED $[M(Pc)O]_n$ MATERIALS. [a]

Compound	$\sigma(\text{ohm cm})^{-1}$ [b]	Activation Energy (eV)	Interplanar Spacing (Å)
$[Si(Pc)O]_n$	3×10^{-8}		3.33(2)
$\{[Si(Pc)O]I_{0.50}\}_n$	2×10^{-2}		
$\{[Si(Pc)O]I_{1.40}\}_n$	2×10^{-1}	0.040 ± 0.001	3.33(2)
$\{[Si(Pc)O]I_{4.60}\}_n$	1×10^{-2}		
$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}		
$[Ge(Pc)O]_n$	$< 10^{-8}$		3.51(2)
$\{[Ge(Pc)O]I_{1.80}\}_n$	3×10^{-2}	0.080 ± 0.006	3.51(2)
$\{[Ge(Pc)O]I_{1.90}\}_n$	5×10^{-2}	0.060 ± 0.003	
$\{[Ge(Pc)O]I_{1.94}\}_n$	6×10^{-2}	0.050 ± 0.007	
$\{[Ge(Pc)O]I_{2.0}\}_n$	1×10^{-1}		
$[Sn(Pc)O]_n$	$< 10^{-8}$		3.95(2)
$\{[Sn(Pc)O]I_{1.2}\}_n$	1×10^{-6}		3.95(2)
$\{[Sn(Pc)O]I_{5.5}\}_n$	2×10^{-4}	0.68 ± 0.01	

[a] Four-probe van der Pauw techniques.

[b] At 300 °K.

Figure 1. Scheme for the assembly and partial oxidation of metallo-
macrocyclic face-to-face polymers.

$-\text{H}_2\text{O}$

$\xrightarrow{\text{I}_2}$ $[(\text{MPcO})\text{I}_x]_n$
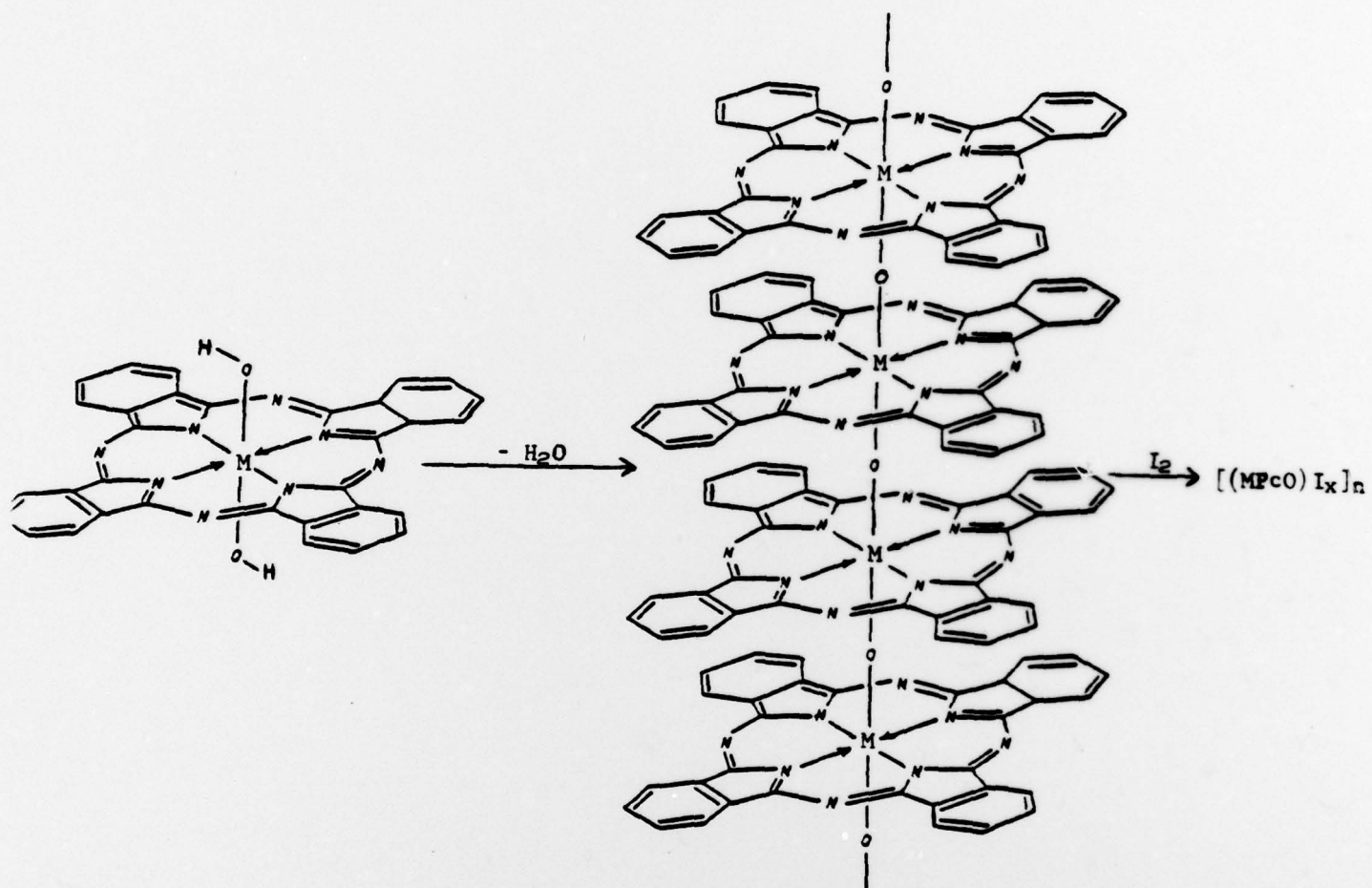
M = Si, Ge, Sn

Figure 2. Resonance Raman spectra of iodinated polymers with 5145 Å (Ar^+) excitation.

$\{[Sn(Pc)O]I_{1.20}\}_n$

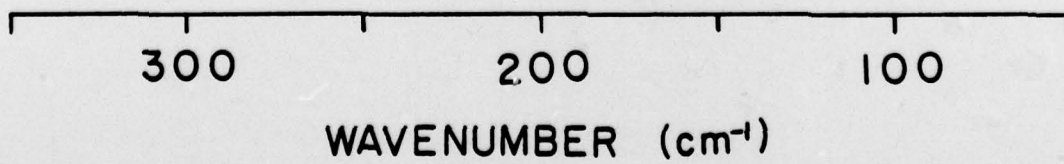$\{[Ge(Pc)O]I_{1.80}\}_n$

$\{[Si(Pc)O]I_{1.94}\}_n$

WAVENUMBER (cm^{-1})

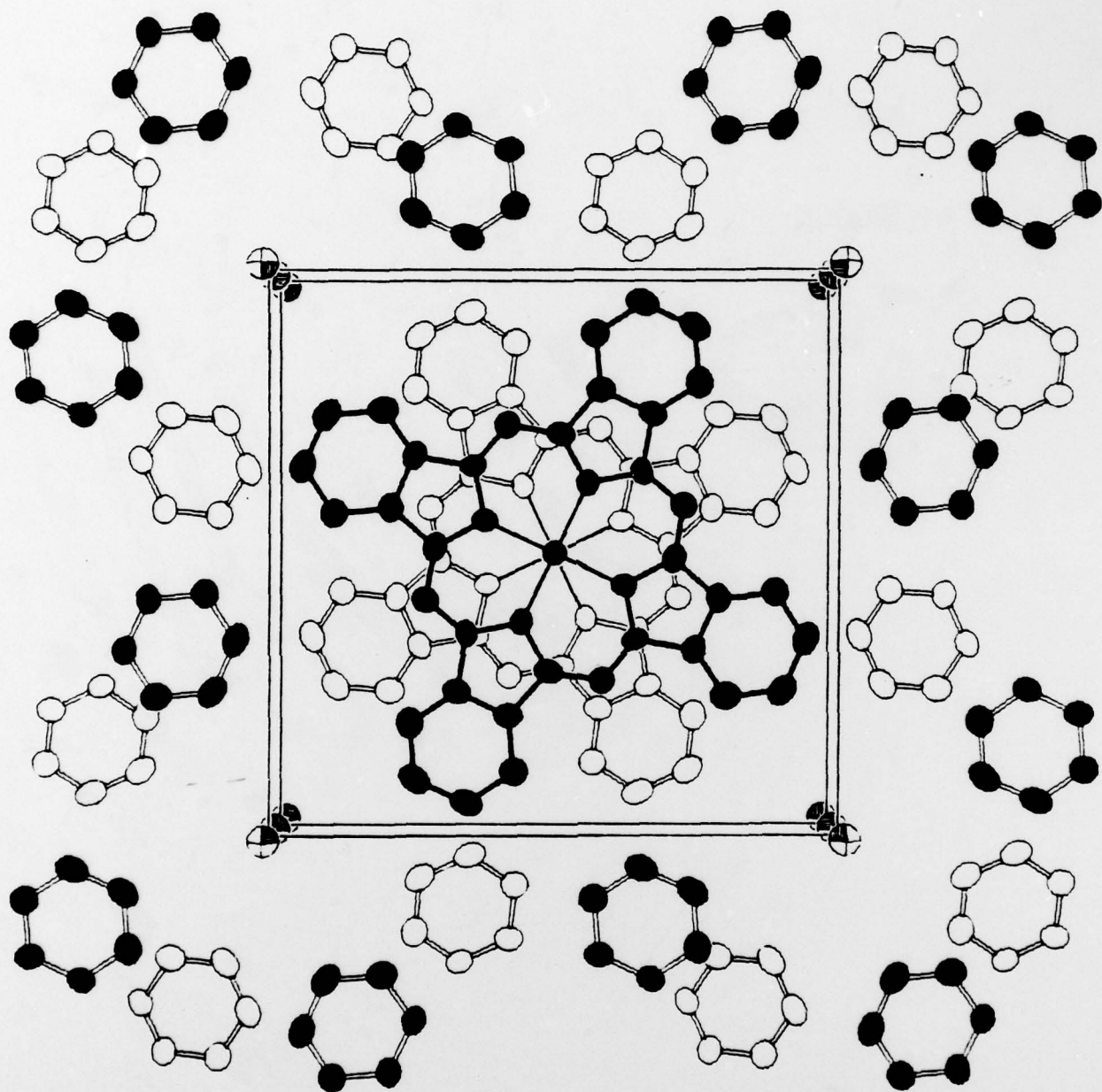Figure 3. Crystal structural of Ni(Pc)I$_{1.0}$ viewed along the stacking direction. From reference 6c.

Figure 4. Crystal structure of $[(CH_3)_3SiO]_2(CH_3)SiO[Si(Pc)O]_3Si(CH_3)-[OSi(CH_3)_3]_2$ from reference 16.
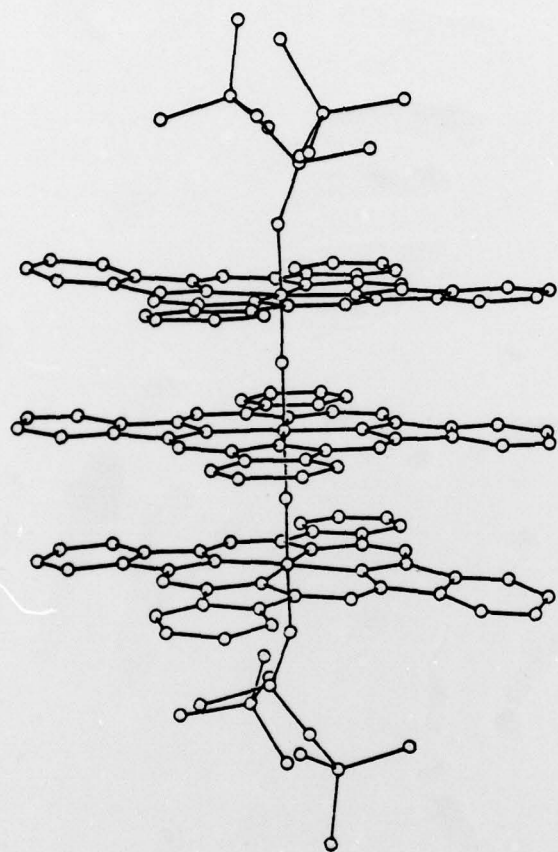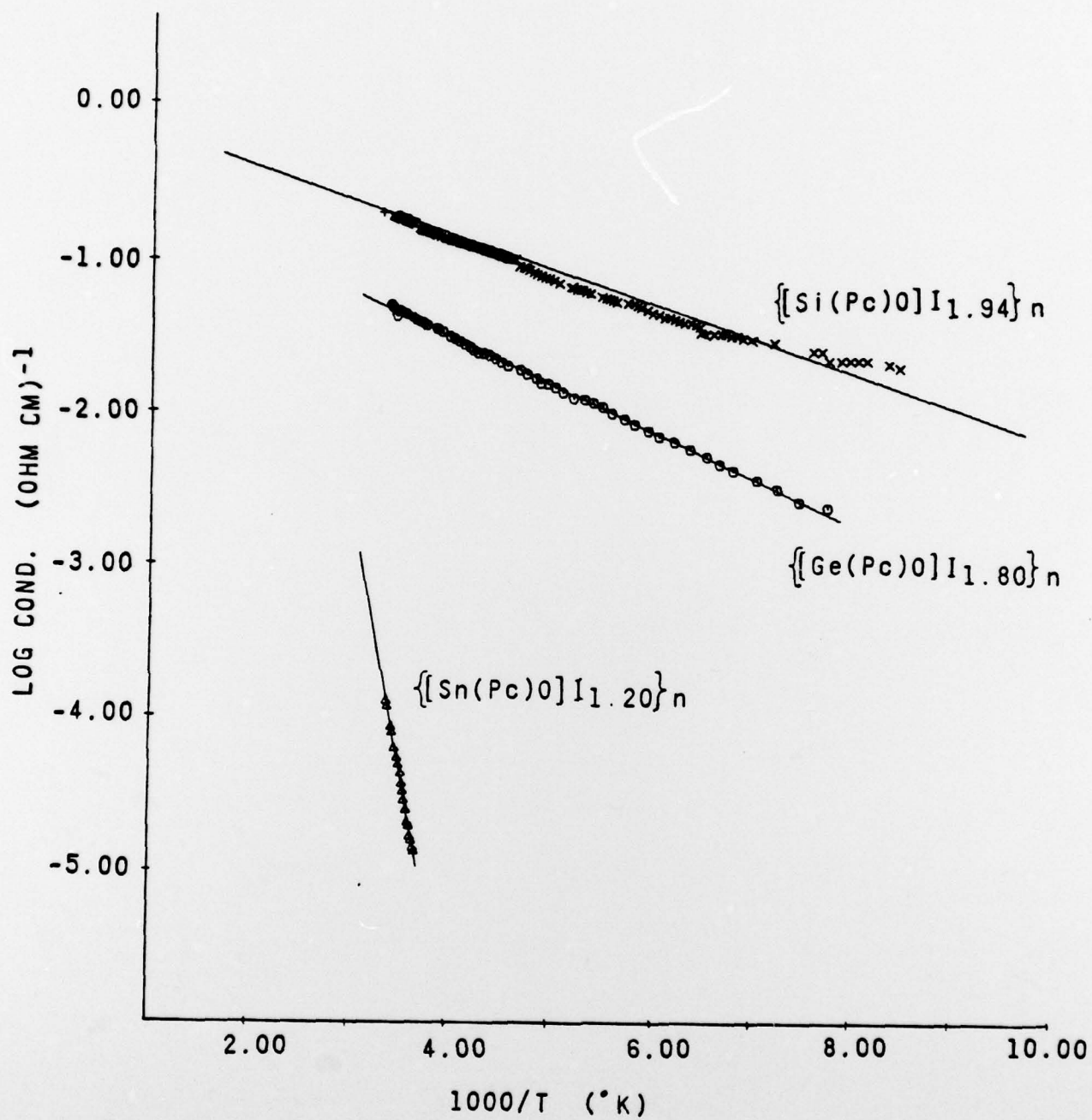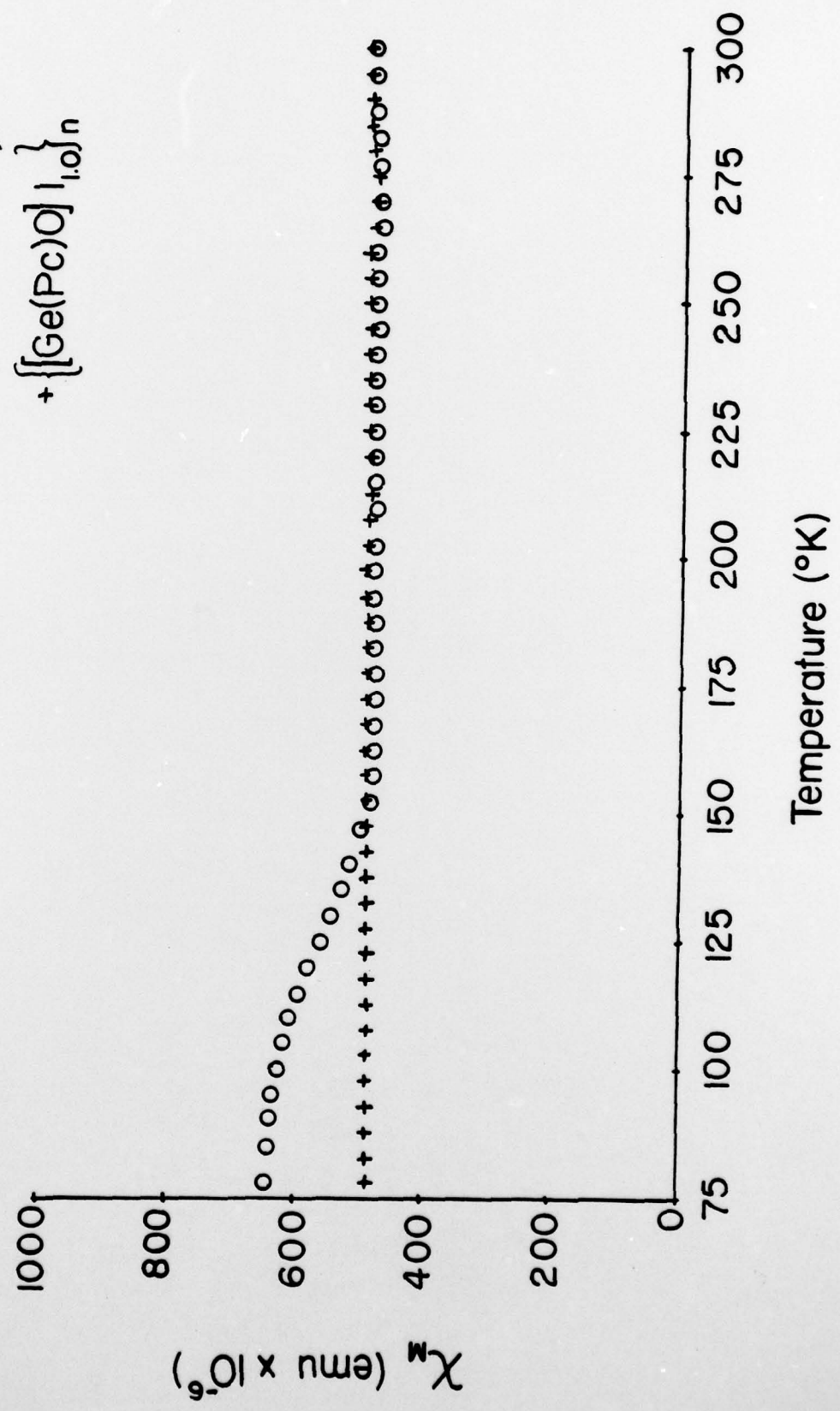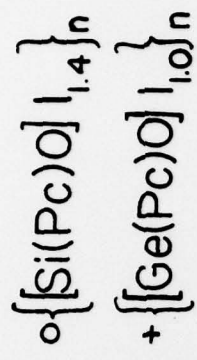
Figure 5.   Four-probe electrical conductivity data for samples of iodine-doped cofacial polymers as compressed pellets.   Solid lines represent a least-squares fit to equation (1).

Figure 6. Variable temperature magnetic susceptibility data for iodine-doped polymers.

χ_M (emu x 10^{-6}) versus Temperature (°K)

o {[Si(Pc)O] I$_{1.4}$}$_n$

+ {[Ge(Pc)O] I$_{1.0}$}$_n$

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